John E. McMurry • Robert C. Fay

General Chemistry: Atoms First

Chapter 10
Liquids, Solids, and Phase Changes

Lecture Notes

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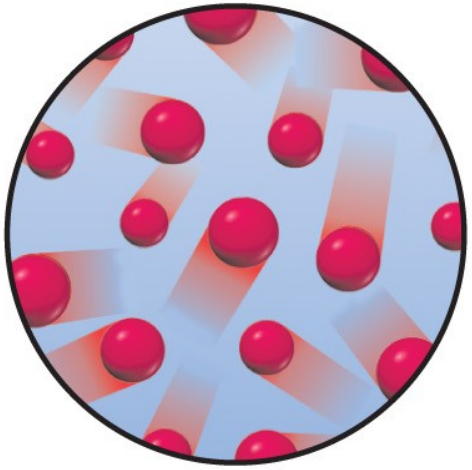
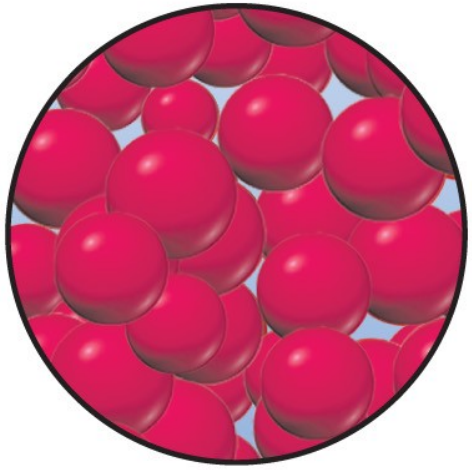
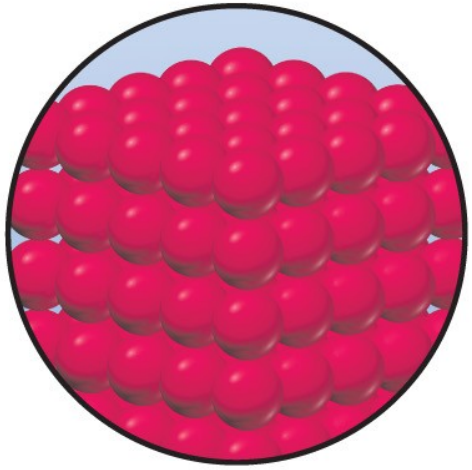


In **gases,** the particles feel little attraction for one another and are free to move about randomly.

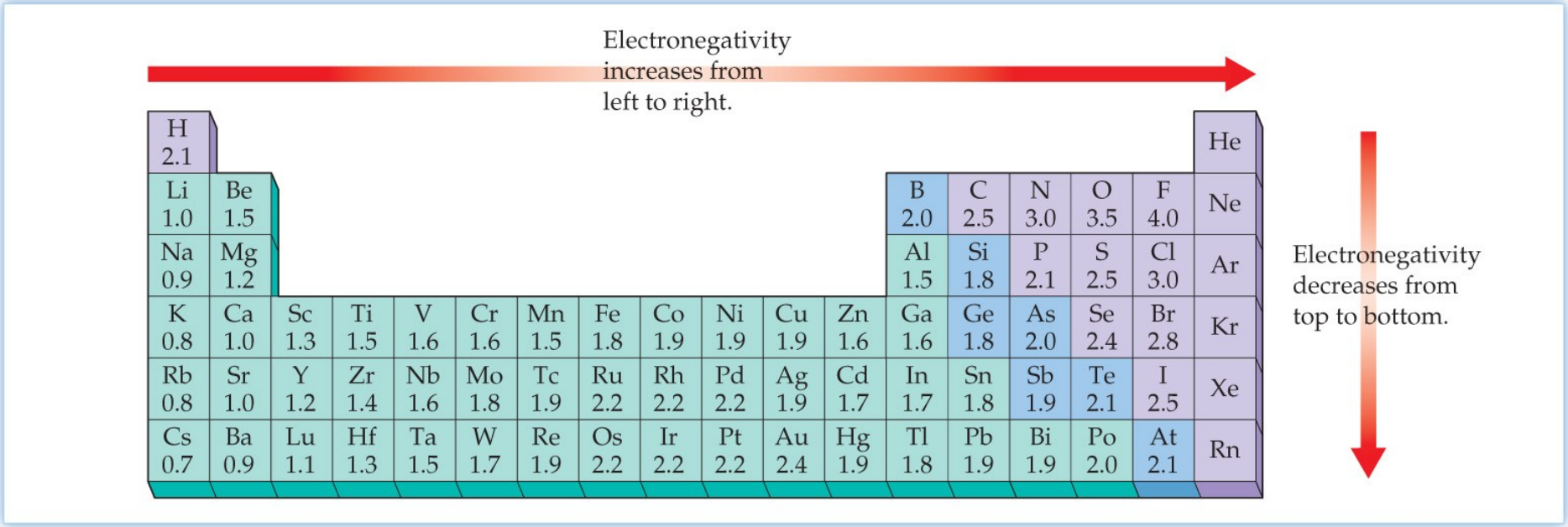


In **liquids,** the particles are held close together by attractive forces but are free to move around one another.



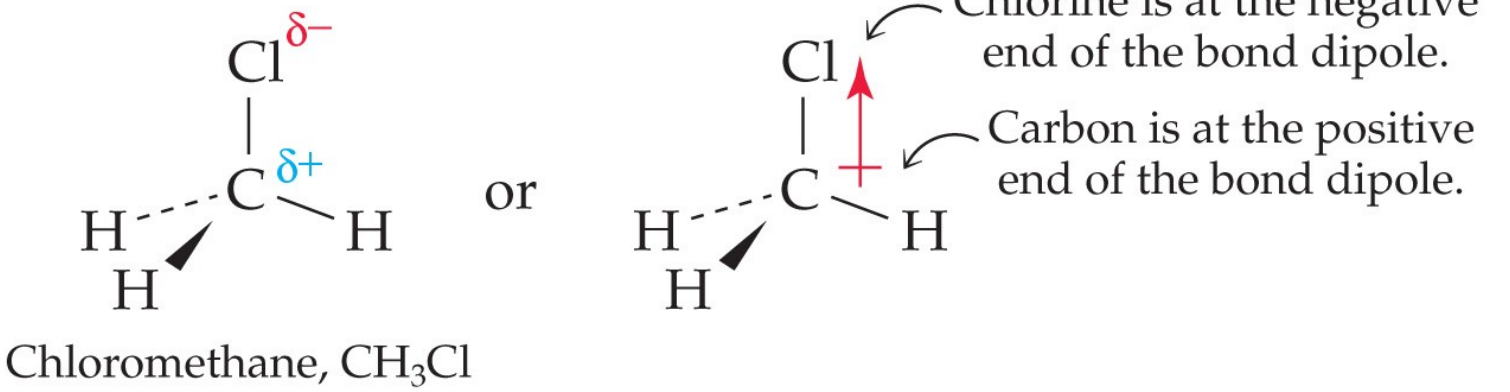
In **solids,** the particles are rigidly held in an ordered arrangement.

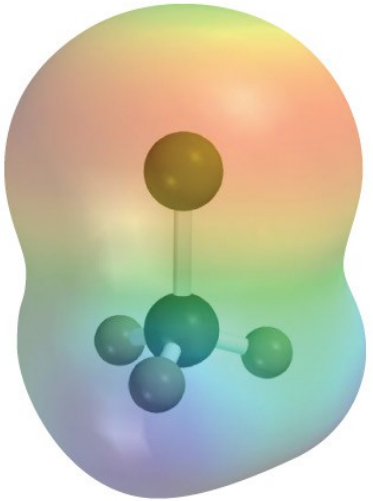
Polar Covalent Bonds and Dipole Moments



H 2.1																He
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe
Cs 0.7	Ba 0.9	Lu 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.1	Rn

Polar Covalent Bonds and Dipole Moments





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C-Cl bond has a **bond dipole** because of a difference in electronegativities.

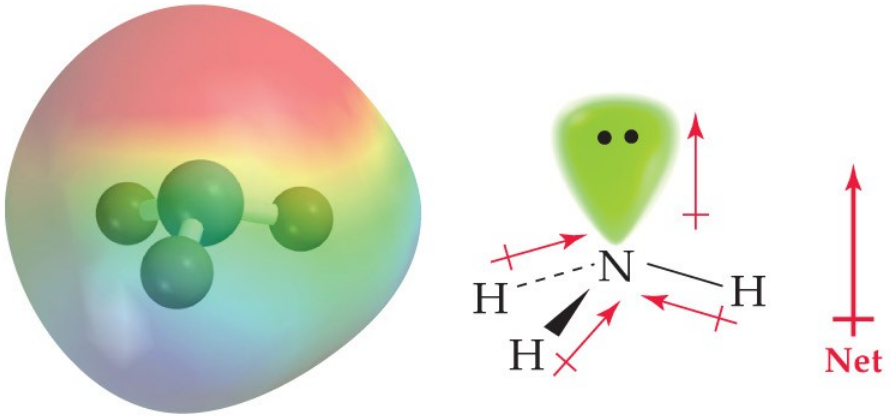
Polar Covalent Bonds and Dipole Moments

TABLE 10.1 Dipole Moments of Some Common Compounds

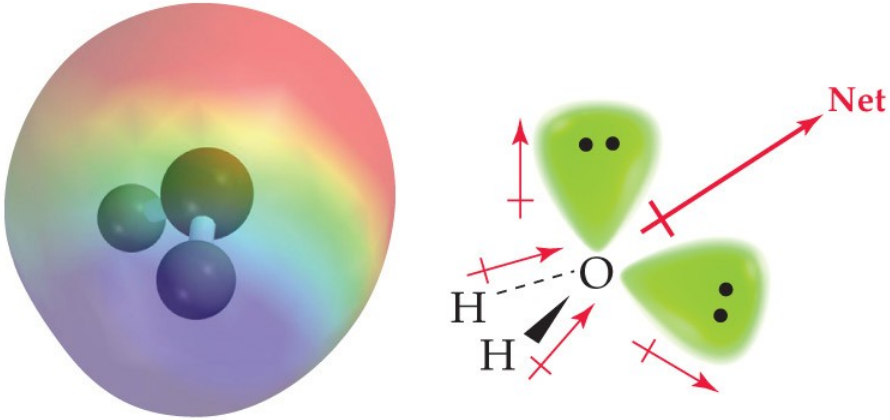
Compound	Dipole Moment (D)
NaCl*	9.0
CH_3Cl	1.90
H_2O	1.85
NH_3	1.47
HCl	1.11
CO_2	0
CCl_4	0

* Measured in the gas phase

Polar Covalent Bonds and Dipole Moments



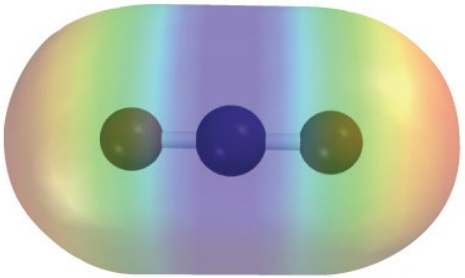
Ammonia (μ = 1.47 D)

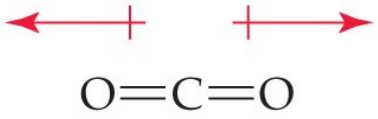


Water (μ = 1.85 D)

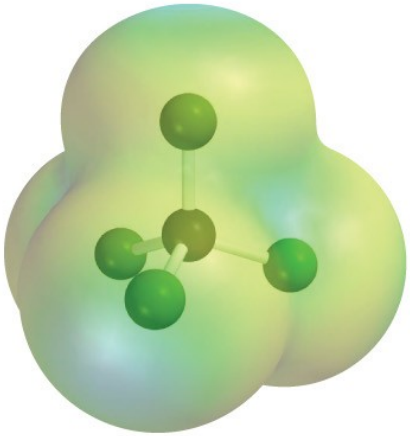
The individual bond polarities **do not** cancel. Therefore, the molecule has a dipole moment. In other words, the molecule is **polar**.

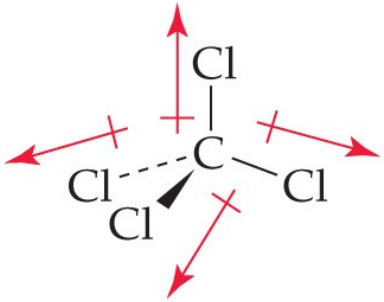
Polar Covalent Bonds and Dipole Moments





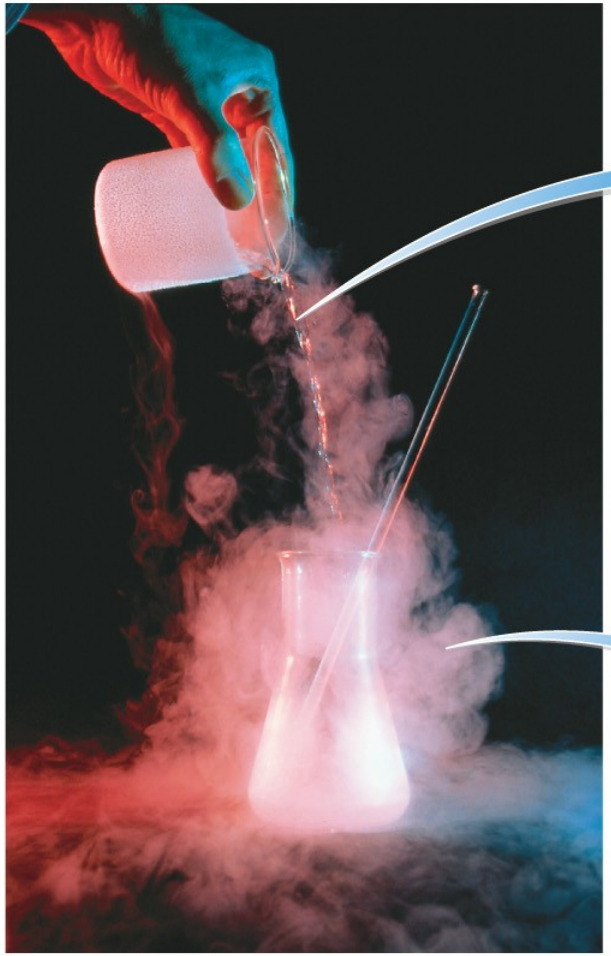
Carbon dioxide ($\mu = 0$)

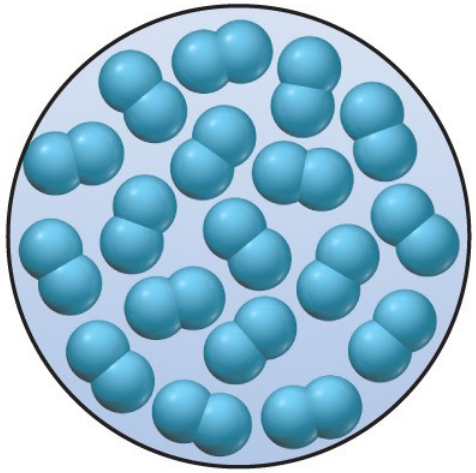




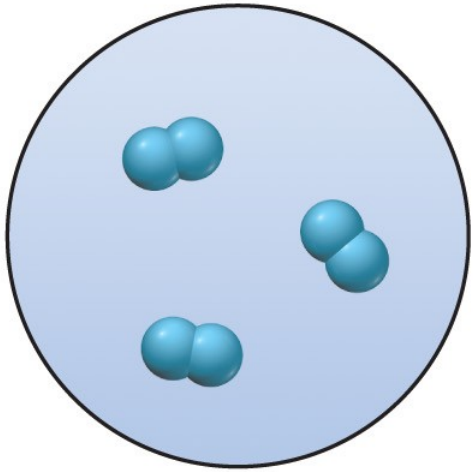
Tetrachloromethane ($\mu = 0$)

The individual bond polarities cancel. Therefore, the molecule does not have a dipole moment. In other words, the molecule is **nonpolar**.





N_2 molecules are weakly attracted to one another at **low temperature** by intermolecular forces, causing nitrogen to become liquid.



At **higher temperatures,** intermolecular forces are no longer able to keep molecules close together, so nitrogen becomes a gas.

Intermolecular Forces

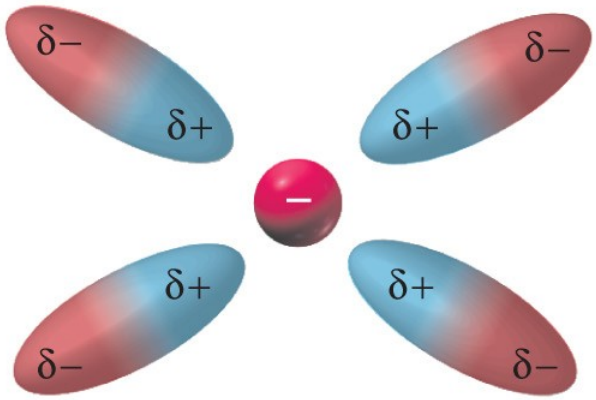
Intermolecular Forces: Attractions between “molecules” that hold them together. These forces are electrical in origin and result from the mutual attraction of unlike charges or the mutual repulsion of like charges.

Types of Intermolecular Forces:

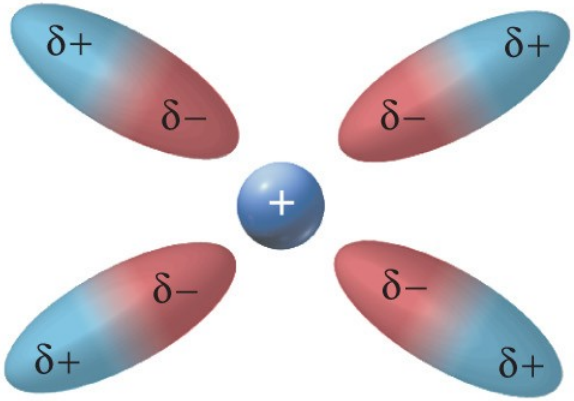
- **Ion-Dipole Forces**
- **Van der Waals Forces**
  - dipole-dipole forces
  - London dispersion forces
  - hydrogen bonds

Intermolecular Forces

Ion-Dipole Forces: The result of electrical interactions between an ion and the partial charges on a polar molecule.



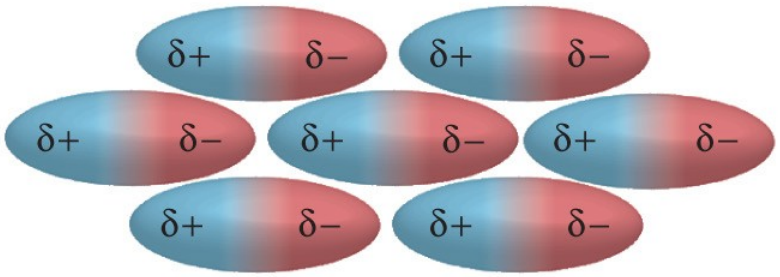
Polar molecules orient toward ions so that the **positive end** of the dipole is near an **anion** and …



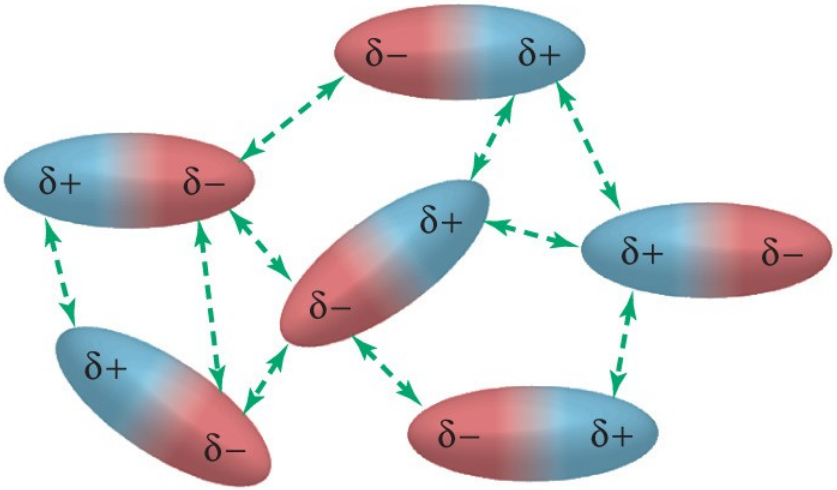
… the **negative end** of the dipole is near a **cation.**

Intermolecular Forces

Dipole-Dipole Forces: The result of electrical interactions between dipoles on neighboring



Polar molecules attract one another when they orient with unlike charges close together, but …



… they repel one another when they orient with like charges together.

Intermolecular Forces

Dipole-Dipole Forces

TABLE 10.2 Comparison of Molecular Masses, Dipole Moments, and Boiling Points

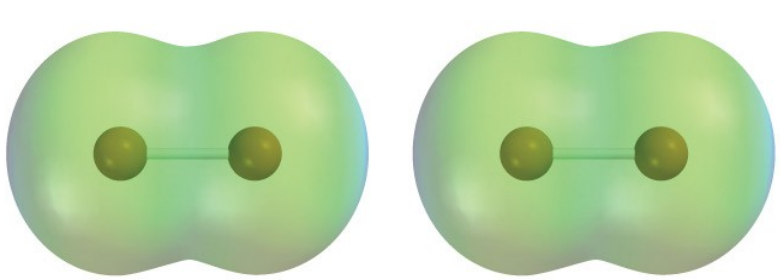
Substance	Mol Mass (amu)	Dipole Moment (D)	bp (K)
$CH_3CH_2CH_3$	44.10	0.08	231
CH_3OCH_3	46.07	1.30	248
CH_3Cl	50.49	1.90	249
CH_3CN	41.05	3.93	355

As the *dipole forces* increase the *intermolecular forces* increase.

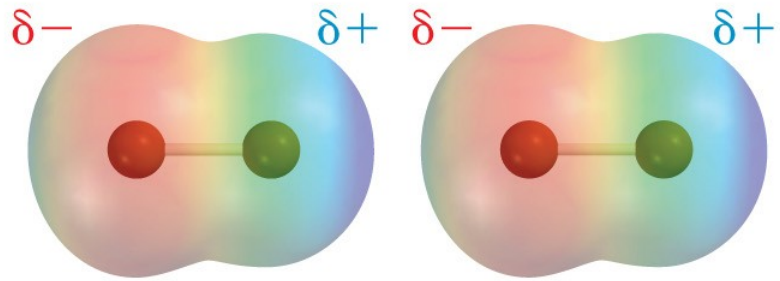
As the *intermolecular forces* increase,

Intermolecular Forces

London Dispersion Forces: The result of motion of electrons which gives the molecule a short-lived dipole moment which induces temporary dipoles in neighboring molecules.



Averaged over time, the electron distribution in a Br_2 molecule is **symmetrical.**



At any given instant, the electron distribution in a molecule may be **unsymmetrical,** resulting in a temporary dipole and inducing a complementary attractive dipole in neighboring molecules.

Intermolecular Forces

London Dispersion Forces

TABLE 10.3 Melting Points and Boiling Points of the Halogens

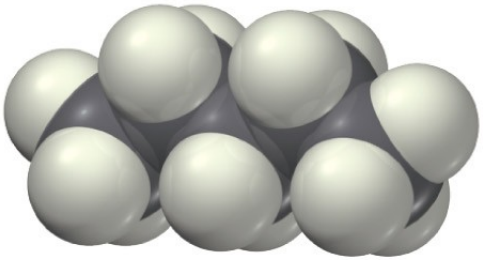
Halogen	mp (K)	bp (K)
F_2	53.5	85.0
Cl_2	171.6	239.1
Br_2	265.9	331.9
I_2	386.8	457.5

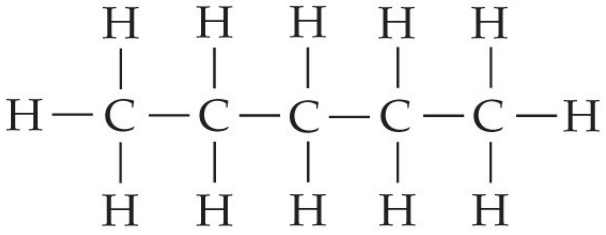
As the *dispersion forces* increase
the *intermolecular forces*
increase.

As the *intermolecular forces*
increase,
the *boiling points* increase.

Intermolecular Forces

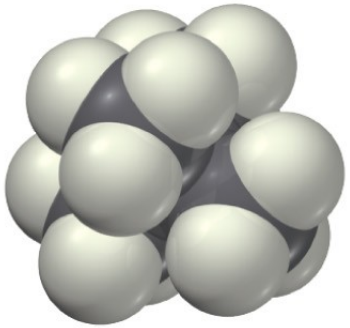
London Dispersion Forces

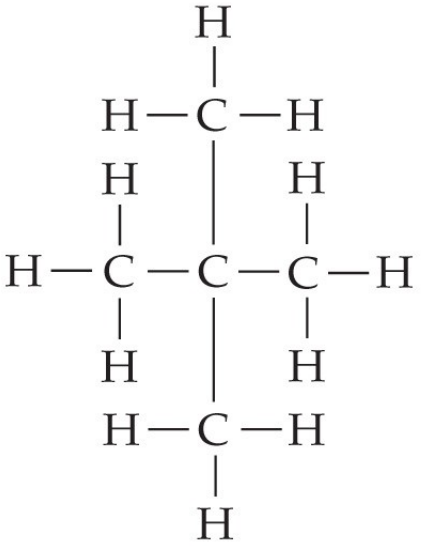




Pentane (bp = 309.2 K)

Longer, **less compact molecules** like pentane feel stronger dispersion forces and consequently have higher boiling points.



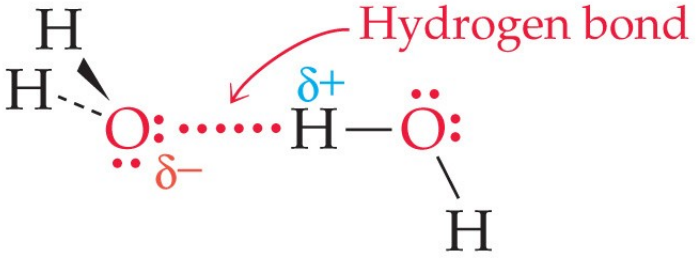


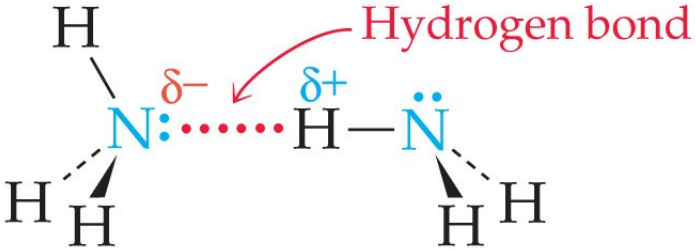
2,2-Dimethylpropane (bp = 282.6 K)

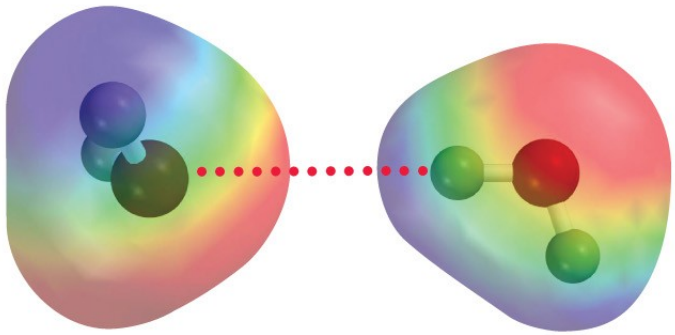
More compact molecules like 2,2-dimethylpropane feel weaker dispersion forces and have lower boiling points.

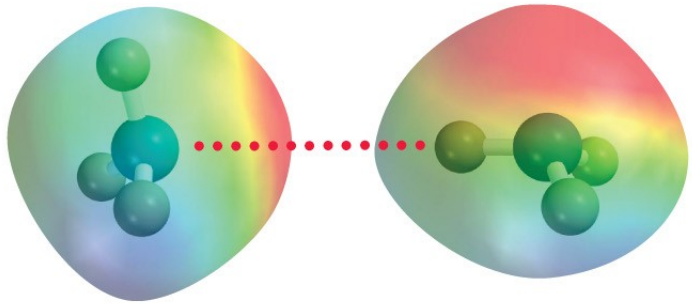
Intermolecular Forces

Hydrogen Bond: An attractive force between a hydrogen atom bonded to a very electronegative atom (O, N, or F) and an unshared electron pair on another electronegative atom





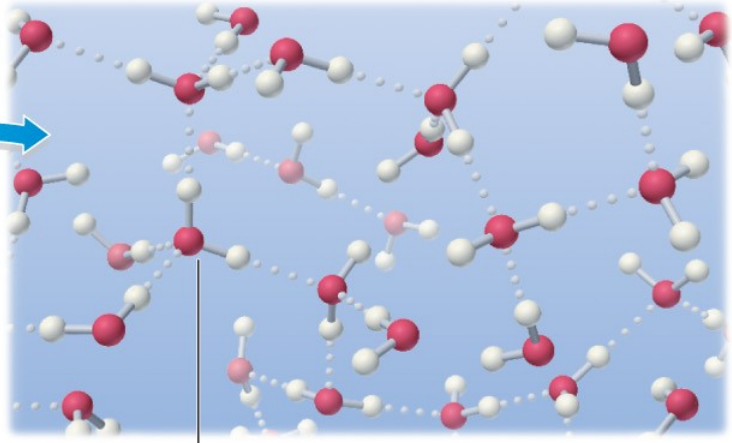




Intermolecular Forces

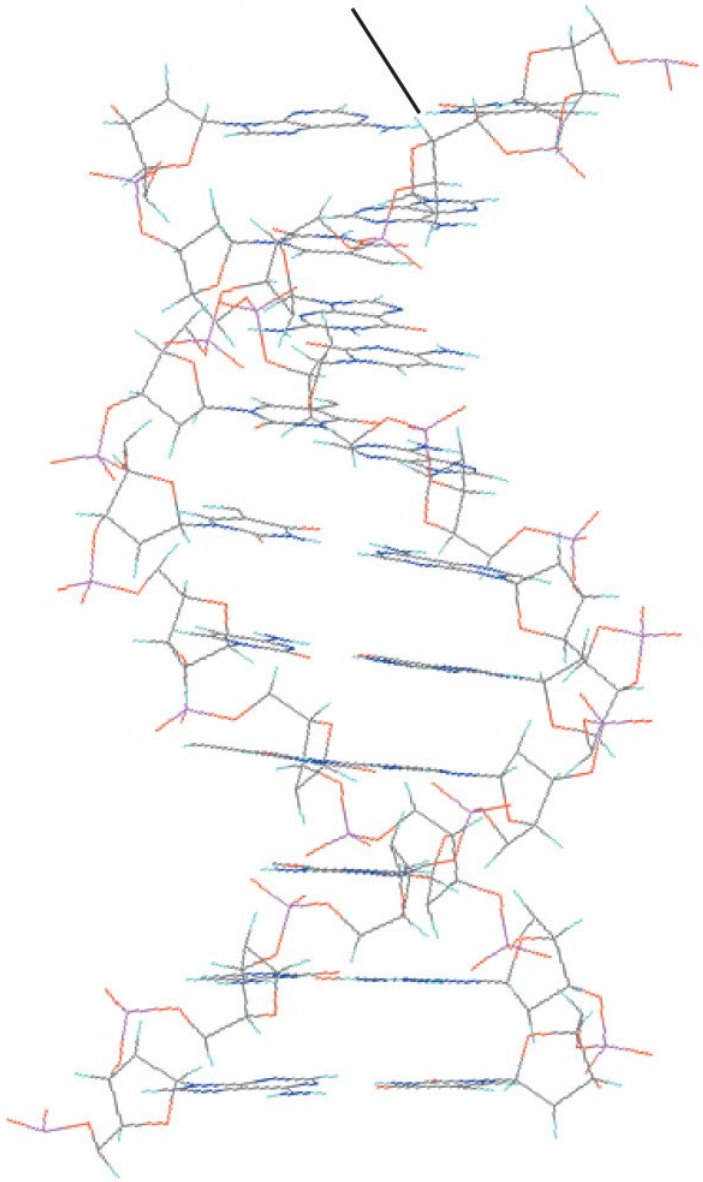
Hydrogen Bond

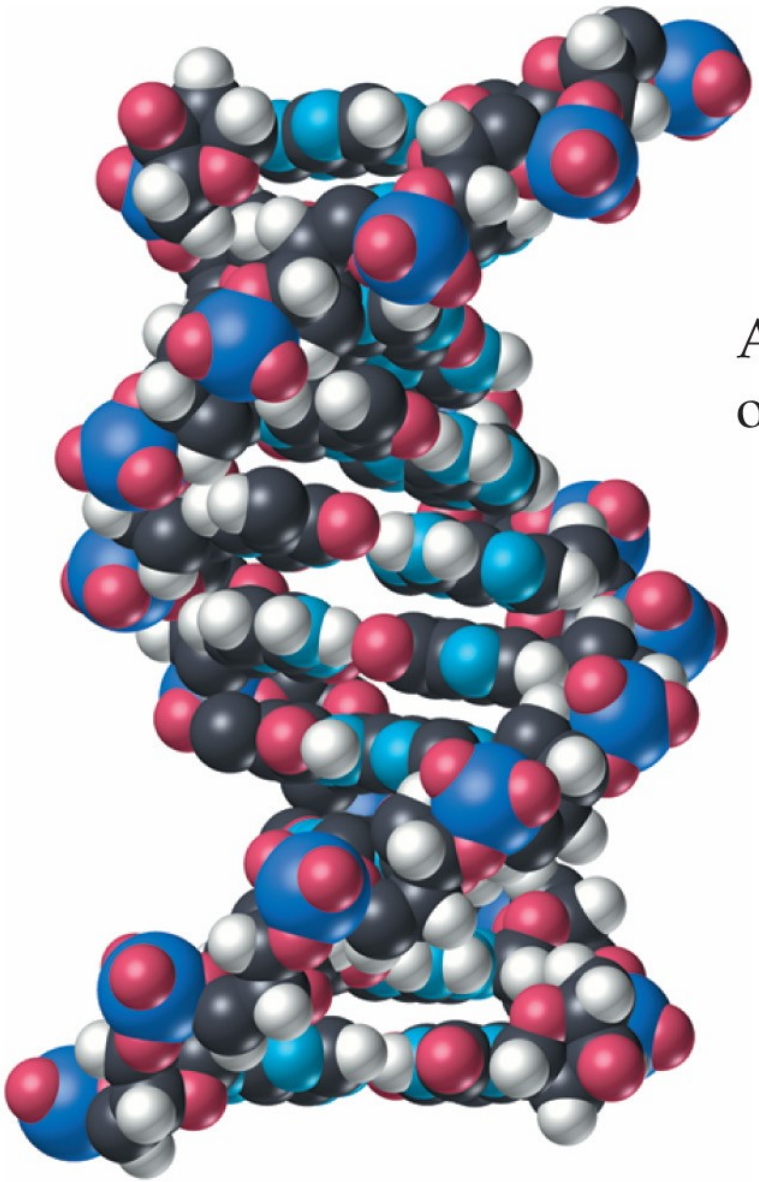
Liquid water contains a vast three-dimensional network of hydrogen bonds resulting from the attraction between positively polarized **hydrogens** and electron pairs on negatively polarized **oxygens.**



An **oxygen** can form two hydrogen bonds, represented by dotted lines.

Hydrogen bond
between chains



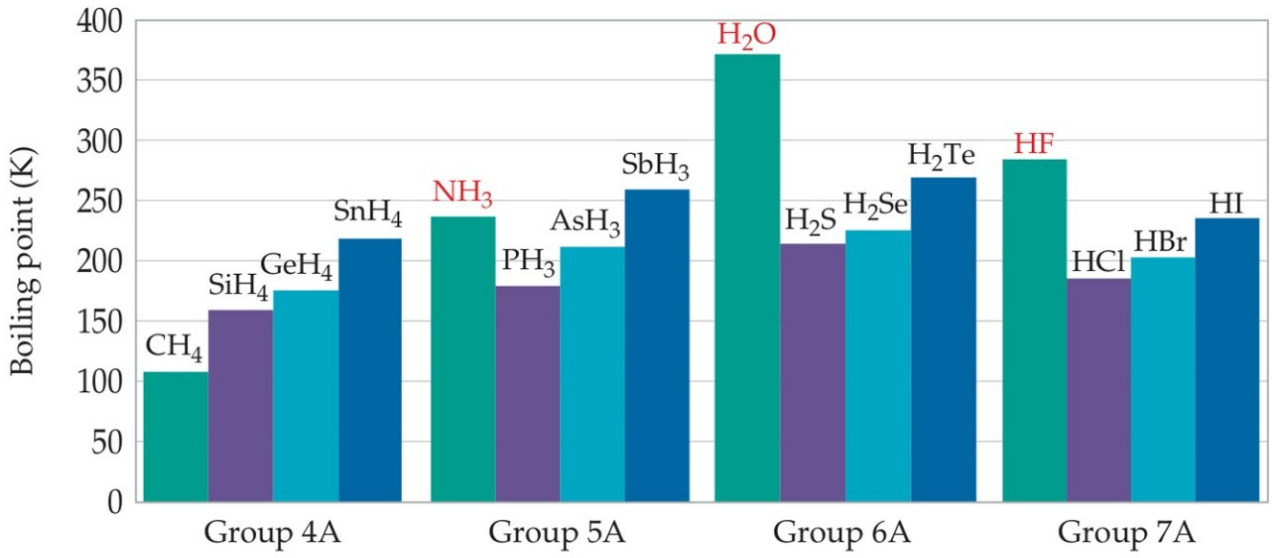


A short segment
of DNA

Intermolecular Forces

Hydrogen Bond

TABLE 10.4 Boiling Points of the Covalent Binary Hydrides of Groups 4A, 5A, 6A, and 7A



The boiling points generally increase with increasing molecular mass down a group of the periodic table, but the hydrides of nitrogen **(NH_3)**, oxygen **(H_2O)**, and fluorine **(HF)** have abnormally high boiling points because these molecules form hydrogen bonds.

Intermolecular Forces

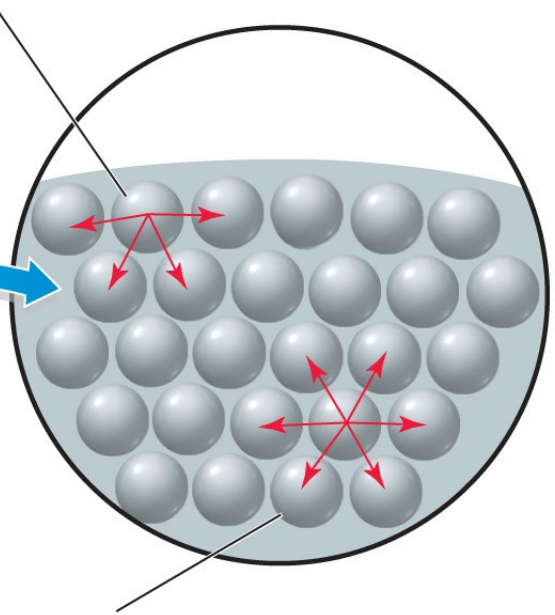
TABLE 10.5 A Comparison of Intermolecular Forces

Force	Strength	Characteristics
Ion–dipole	Moderate (10–50 kJ/mol)	Occurs between ions and polar solvents
Dipole–dipole	Weak (3–4 kJ/mol)	Occurs between polar molecules
London dispersion	Weak (1–10 kJ/mol)	Occurs between all molecules; strength depends on size, polarizability
Hydrogen bond	Moderate (10–40 kJ/mol)	Occurs between molecules with O—H, N—H, and F—H bonds

Some Properties of Liquids

Some Properties of Liquids

Molecules or atoms on the **surface** feel attractive forces on only one side and are thus drawn in toward the liquid.



Molecules or atoms in the **middle** of a liquid are attracted equally in all directions.

Some Properties of Liquids

TABLE 10.6 Viscosities and Surface Tensions of Some Common Substances at 20 °C

Name	Formula	Viscosity ($N \cdot s/m^2$)	Surface Tension (J/m^2)
Pentane	C_5H_{12}	2.4×10^{-4}	1.61×10^{-2}
Benzene	C_6H_6	6.5×10^{-4}	2.89×10^{-2}
Water	H_2O	1.00×10^{-3}	7.29×10^{-2}
Ethanol	C_2H_5OH	1.20×10^{-3}	2.23×10^{-2}
Mercury	Hg	1.55×10^{-3}	4.6×10^{-1}
Glycerol	$C_3H_5(OH)_3$	1.49	6.34×10^{-2}

Phase Changes

Phase Change (State Change): A change in physical form but not the chemical identity of a substance.

Fusion (melting): solid to liquid

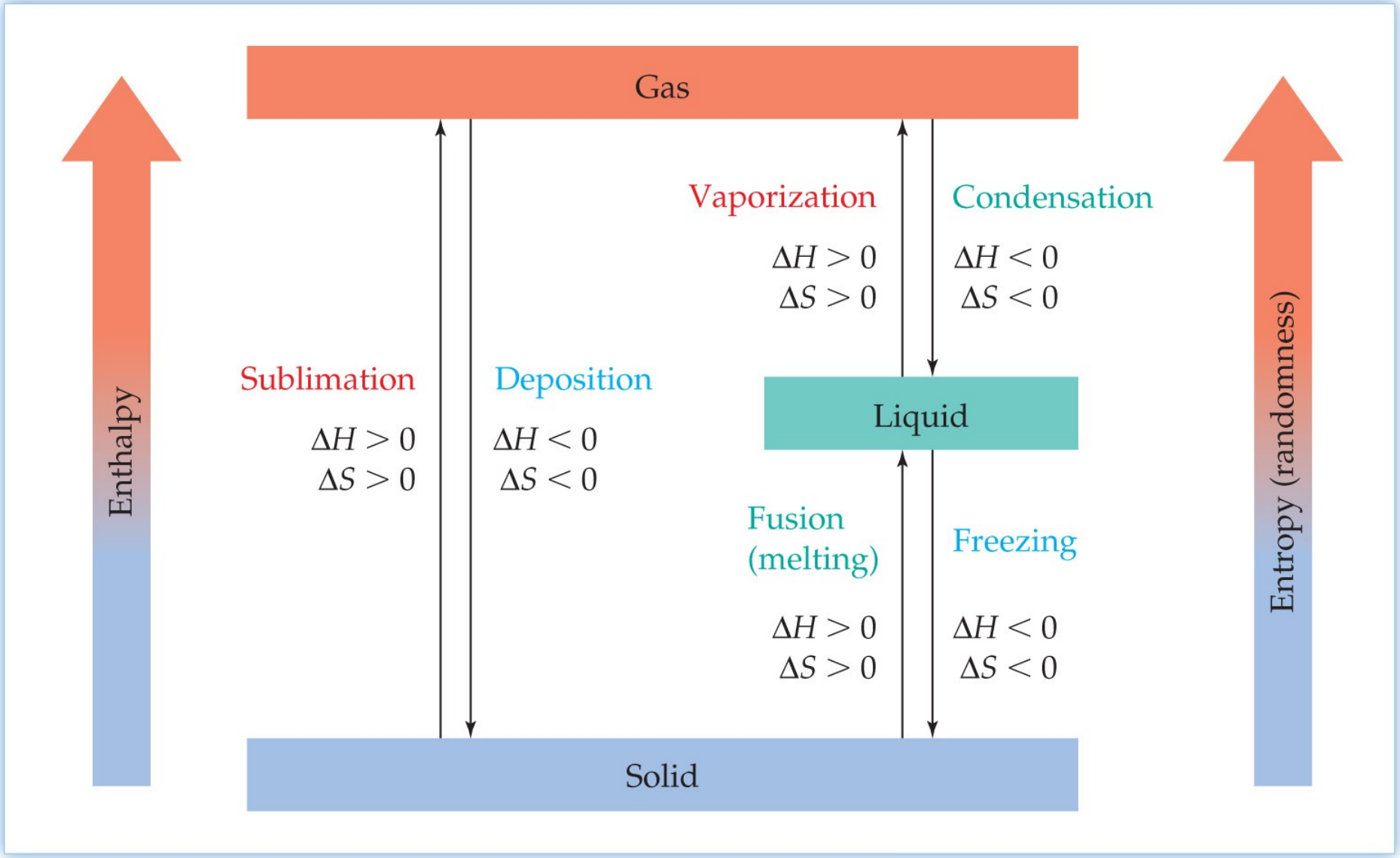
Freezing: liquid to solid

Vaporization: liquid to gas

Condensation: gas to liquid

Sublimation: solid to gas

Deposition: gas to solid


Gas
Liquid
Solid
Enthalpy
Entropy (randomness)
Vaporization
$\Delta H > 0$
$\Delta S > 0$
Condensation
$\Delta H < 0$
$\Delta S < 0$
Sublimation
$\Delta H > 0$
$\Delta S > 0$
Deposition
$\Delta H < 0$
$\Delta S < 0$
Fusion (melting)
$\Delta H > 0$
$\Delta S > 0$
Freezing
$\Delta H < 0$
$\Delta S < 0$

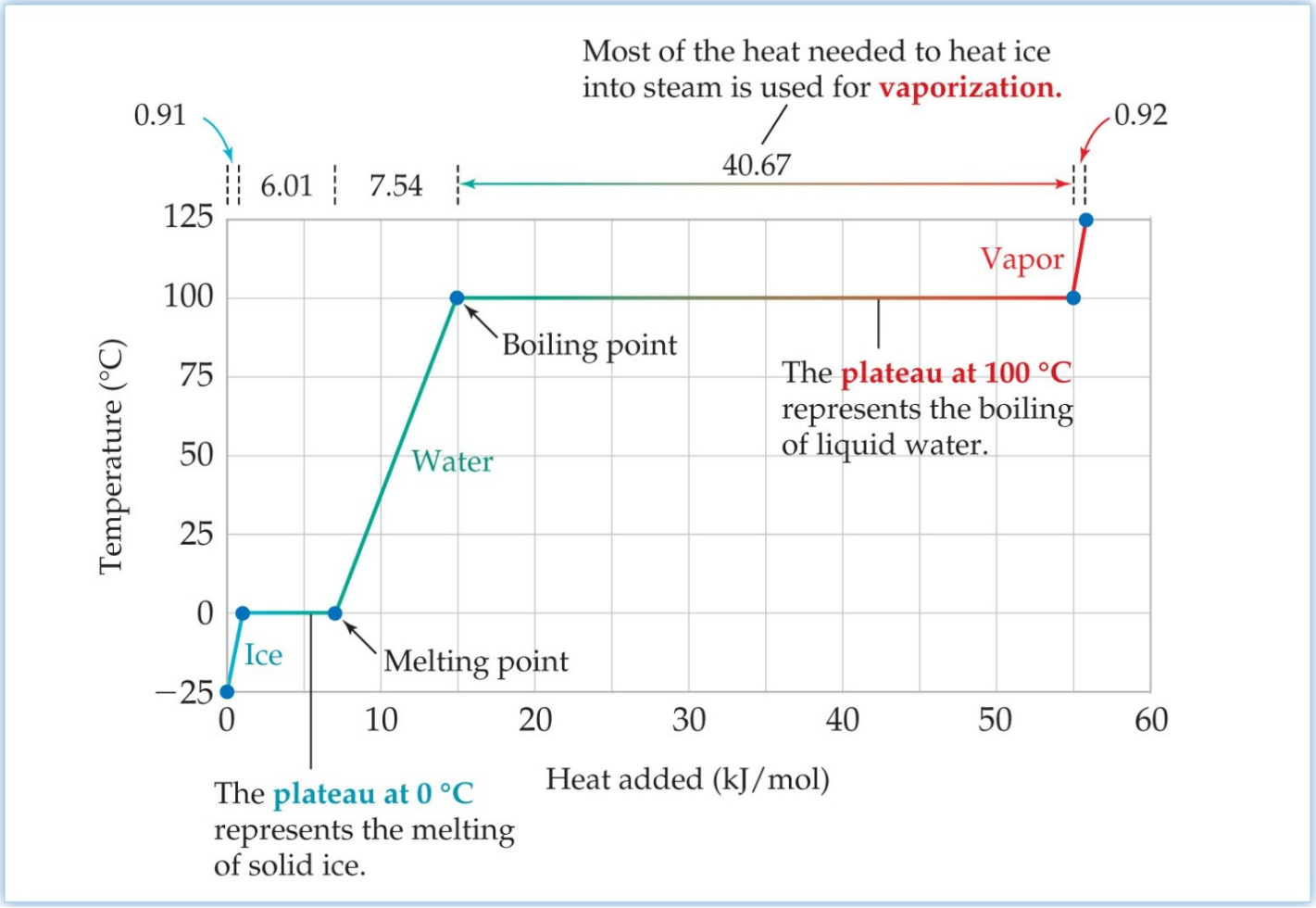
Phase Changes

Enthalpy (Heat) of Fusion (ΔH_{fusion}): The amount of energy required to convert a solid into a liquid.

Enthalpy (Heat) of Vaporization (ΔH_{vap}): The amount of energy required to convert a liquid into a gas.

Phase Changes

Heating Curve for Water



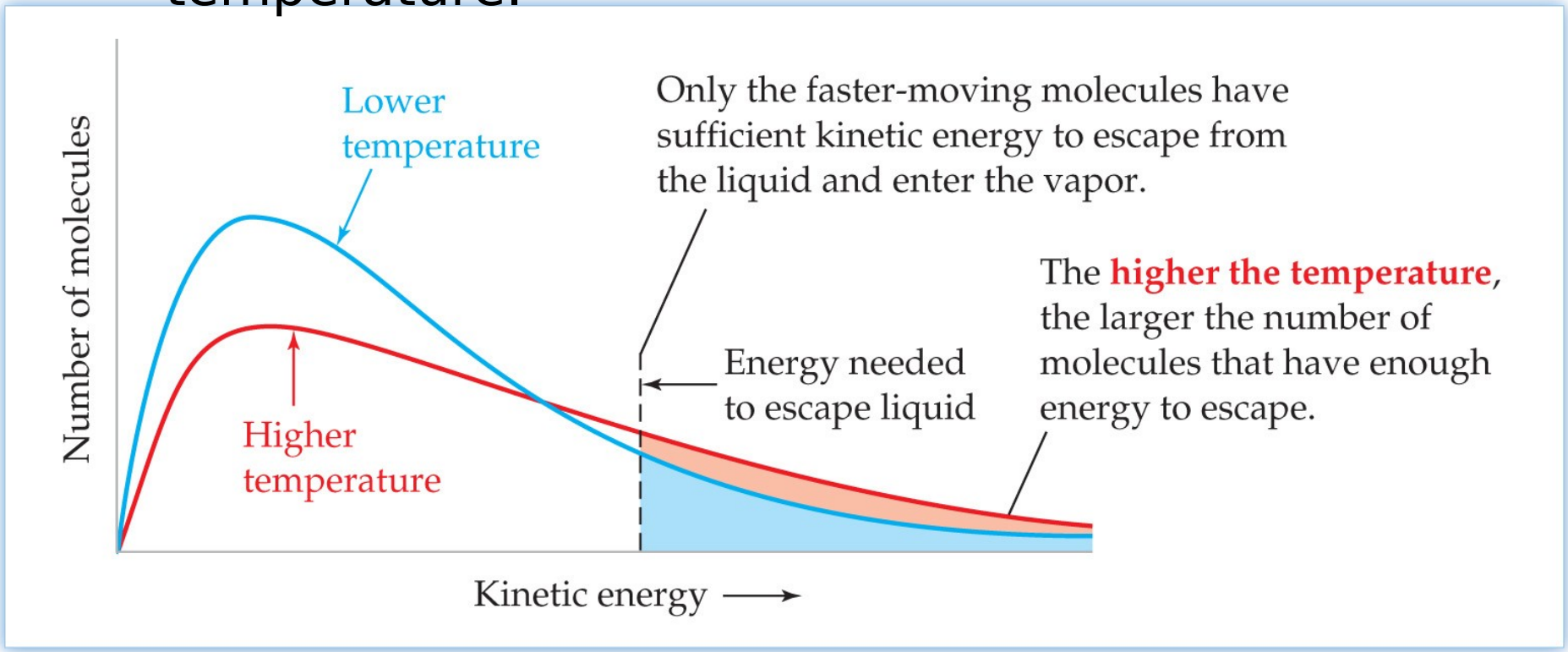
Phase Changes

TABLE 10.7 Heats of Fusion and Heats of Vaporization for Some Common Compounds

Name	Formula	ΔH_{fusion} (kJ/mol)	ΔH_{vap} (kJ/mol)
Ammonia	NH_3	5.66	23.33
Benzene	C_6H_6	9.87	30.72
Ethanol	C_2H_5OH	4.93	38.56
Helium	He	0.02	0.08
Mercury	Hg	2.30	59.11
Water	H_2O	6.01	40.67

Evaporation, Vapor Pressure, and Boiling Point

Vapor Pressure: The partial pressure of a gas in equilibrium with liquid at a constant temperature.


Number of molecules
Lower temperature
Higher temperature
Only the faster-moving molecules have sufficient kinetic energy to escape from the liquid and enter the vapor.
Energy needed to escape liquid
The higher the temperature, the larger the number of molecules that have enough energy to escape.
Kinetic energy

Evaporation, Vapor Pressure, and Boiling Point

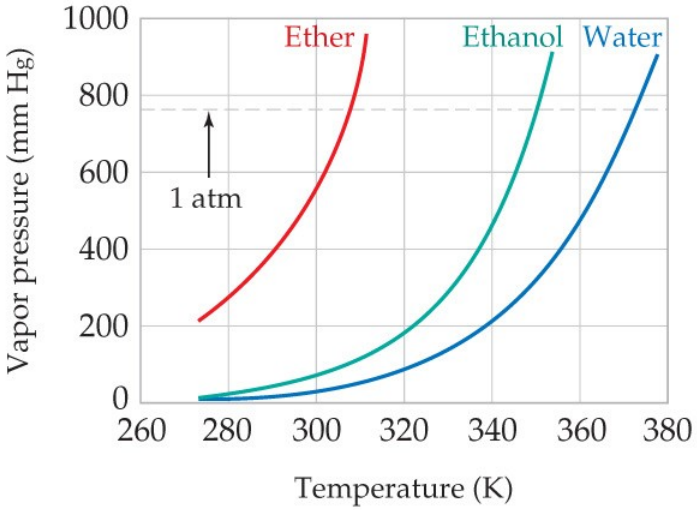
Clausius-Clapeyron Equation

$$\ln P_{\text{vap}} = \left(- \frac{\Delta H_{\text{vap}}}{R} \right) \frac{1}{T} + C$$

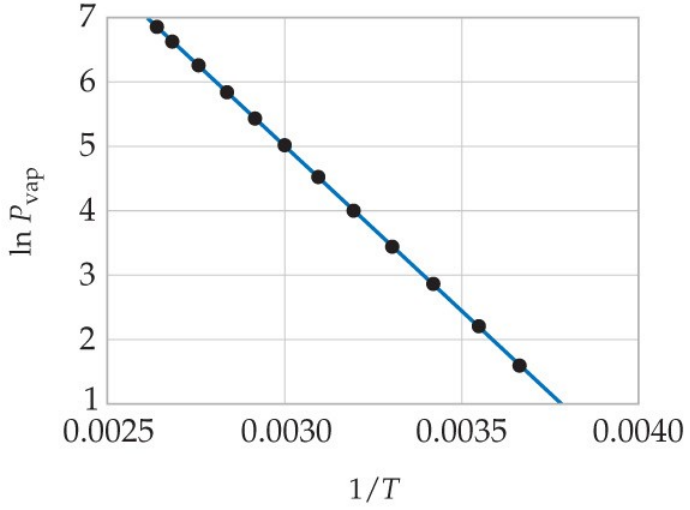
$$y = m x + b$$

TABLE 10.8 Vapor Pressure of Water at Various Temperatures

Temp (K)	P_{vap} (mm Hg)	ln P_{vap}	$1/T$	Temp (K)	P_{vap} (mm Hg)	ln P_{vap}	$1/T$
273	4.58	1.522	0.003 66	333	149.4	5.007	0.003 00
283	9.21	2.220	0.003 53	343	233.7	5.454	0.002 92
293	17.5	2.862	0.003 41	353	355.1	5.872	0.002 83
303	31.8	3.459	0.003 30	363	525.9	6.265	0.002 75
313	55.3	4.013	0.003 19	373	760.0	6.633	0.002 68
323	92.5	4.527	0.003 10	378	906.0	6.809	0.002 65



The vapor pressures of **ether**, **ethanol**, and **water** show a nonlinear rise when plotted as a function of temperature.



A plot of ln P_{vap} versus $1/T$ (Kelvin) for water, prepared from the data in Table 10.8, shows a linear relationship.

Kinds of Solids

Amorphous Solids: Particles are randomly arranged and have no ordered long-range structure. Example - rubber.

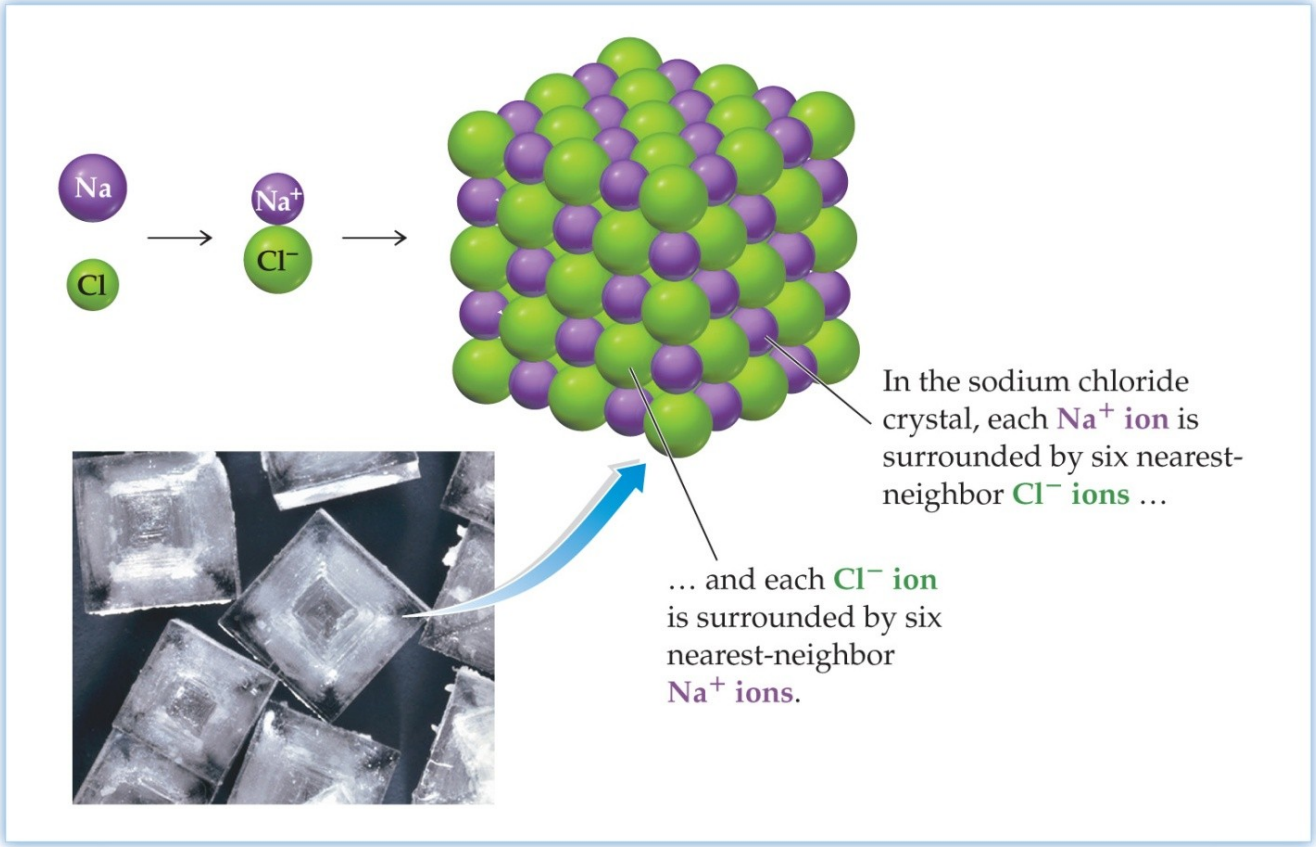
Crystalline Solids: Particles have an ordered arrangement extending over a long range.

- ionic solids
- molecular solids
- covalent network solids
- metallic solids

(a) A crystalline solid, such as this amethyst, has flat faces and distinct angles. These regular macroscopic features reflect a similarly ordered arrangement of particles at the atomic level.

(b) An amorphous solid like rubber has a disordered arrangement of its constituent particles.

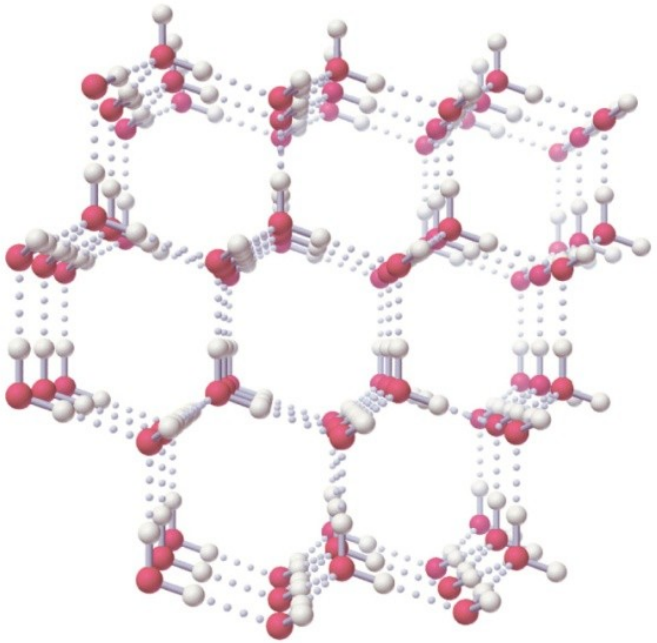
Kinds of Solids


Na
Cl
Na+
Cl−
In the sodium chloride crystal, each Na+ ion is surrounded by six nearest-neighbor Cl− ions …
… and each Cl− ion is surrounded by six nearest-neighbor Na+ ions.

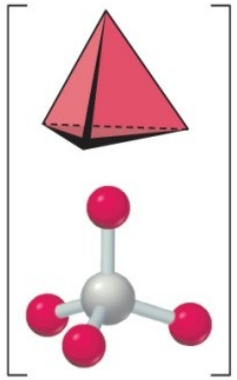
Ionic Solids: Particles are ions ordered in a regular three-dimensional arrangement and held together by ionic bonds. Example - sodium chloride.

Kinds of Solids

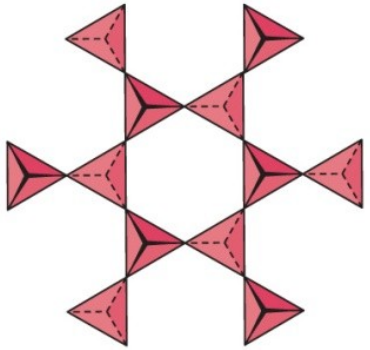
Molecular Solids: Particles are molecules held together by intermolecular forces. Example - ice.



(a) Ice consists of individual H_2O molecules held together in a regular manner by hydrogen bonds.



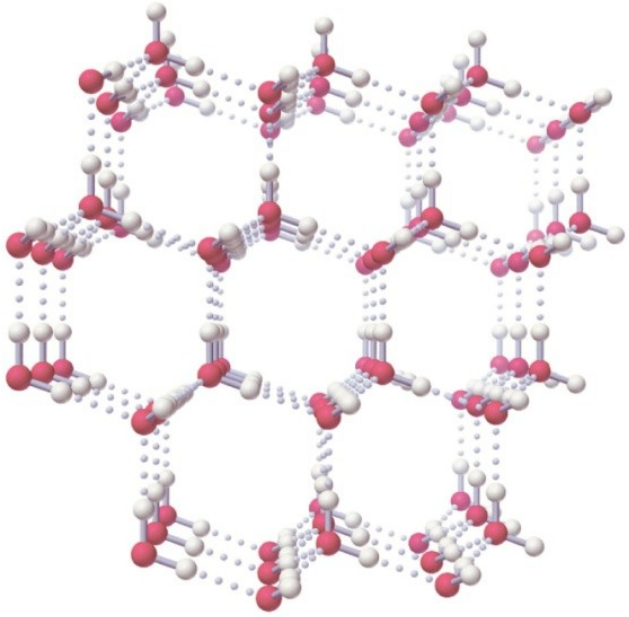
(b) Quartz (SiO_2) is essentially one very large molecule with Si–O covalent bonds. Each silicon atom has tetrahedral geometry and is bonded to four oxygens; each oxygen has approximately linear geometry and is bonded to two silicons.



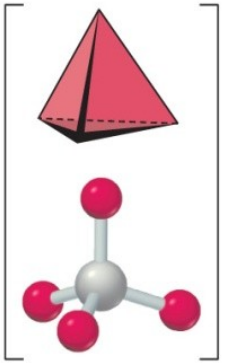
(c) This shorthand representation shows how SiO_4 tetrahedra join at their corners to share oxygen atoms.

Kinds of Solids

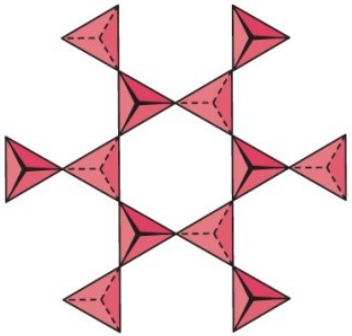
Covalent Network Solids: Particles are atoms linked together by covalent bonds into a giant three-dimensional array.



(a) Ice consists of individual H_2O molecules held together in a regular manner by hydrogen bonds.



(b) Quartz (SiO_2) is essentially one very large molecule with Si–O covalent bonds. Each silicon atom has tetrahedral geometry and is bonded to four oxygens; each oxygen has approximately linear geometry and is bonded to two silicons.



(c) This shorthand representation shows how SiO_4 tetrahedra join at their corners to share oxygen atoms.

Example: quartz

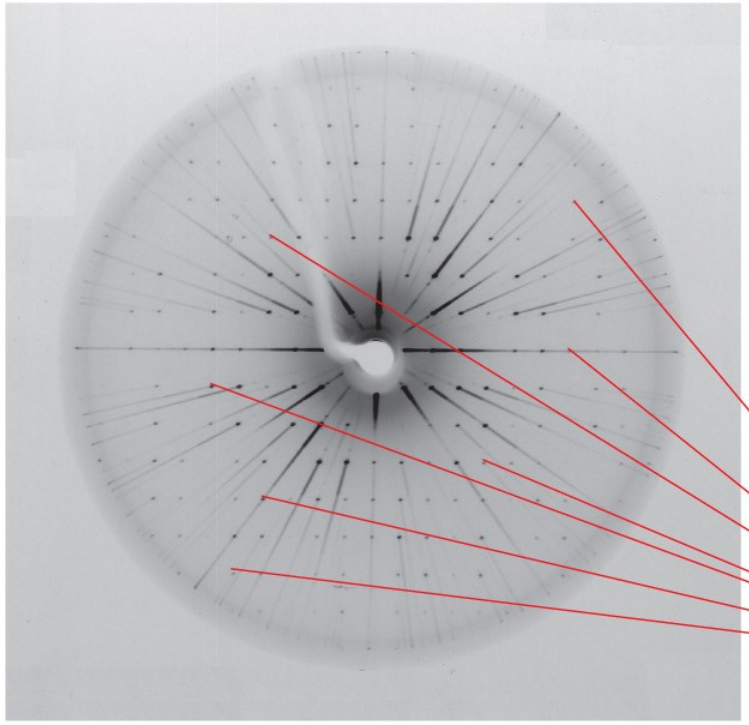
Kinds of Solids

Metallic Solids: Particles are metal atoms whose crystals have metallic properties such as electrical conductivity. Example - iron.

Summary

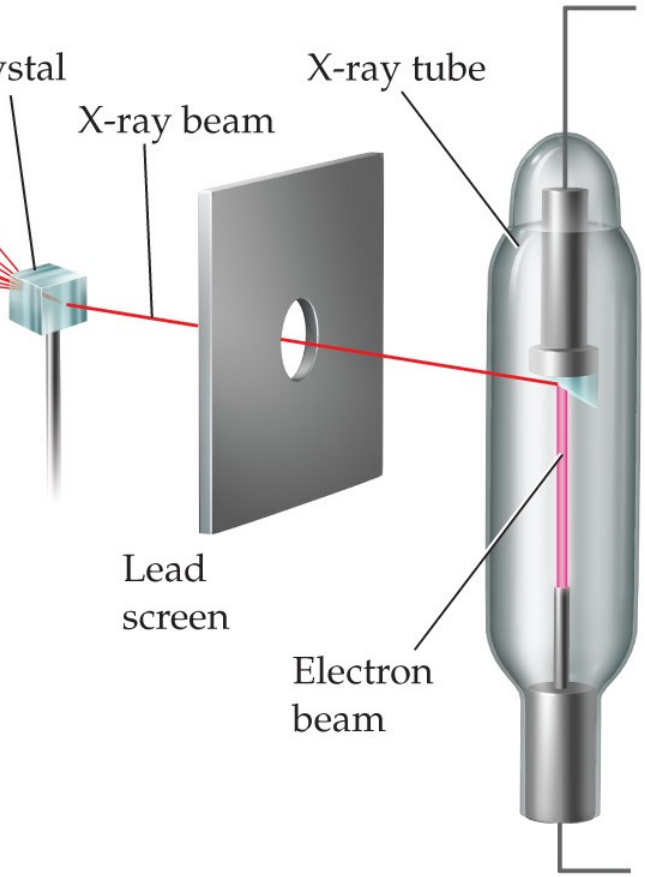
TABLE 10.9 Types of Crystalline Solids and Their Characteristics

Type of Solid	Intermolecular Forces	Properties	Examples
Ionic	Ion–ion forces	Brittle, hard, high-melting	NaCl, KBr, $MgCl_2$
Molecular	Dispersion forces, dipole–dipole forces, hydrogen bonds	Soft, low-melting, nonconducting	H_2O, Br_2, CO_2, CH_4
Covalent network	Covalent bonds	Hard, high-melting	C (diamond), SiO_2
Metallic	Metallic bonds	Variable hardness and melting point, conducting	Na, Zn, Cu, Fe



Photographic film

A beam of X rays impinges on a crystal and allowed to strike a photographic film.

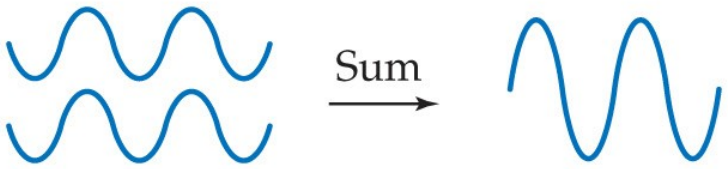


The rays are diffracted by atoms in the crystal, giving rise to a regular pattern of spots on the film.

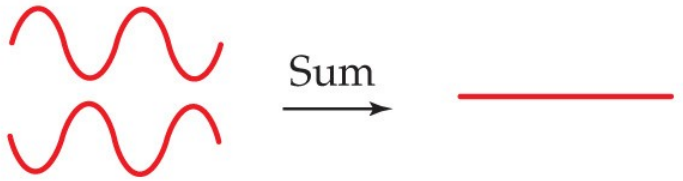
Probing the Structure of Solids: X-Ray Crystallography

Diffraction: Occurs when electromagnetic radiation is scattered by an object containing regularly spaced lines (such as a diffraction grating) or points (such as the atoms in a crystal).

Interference: Occurs when two waves pass through the same region of space.

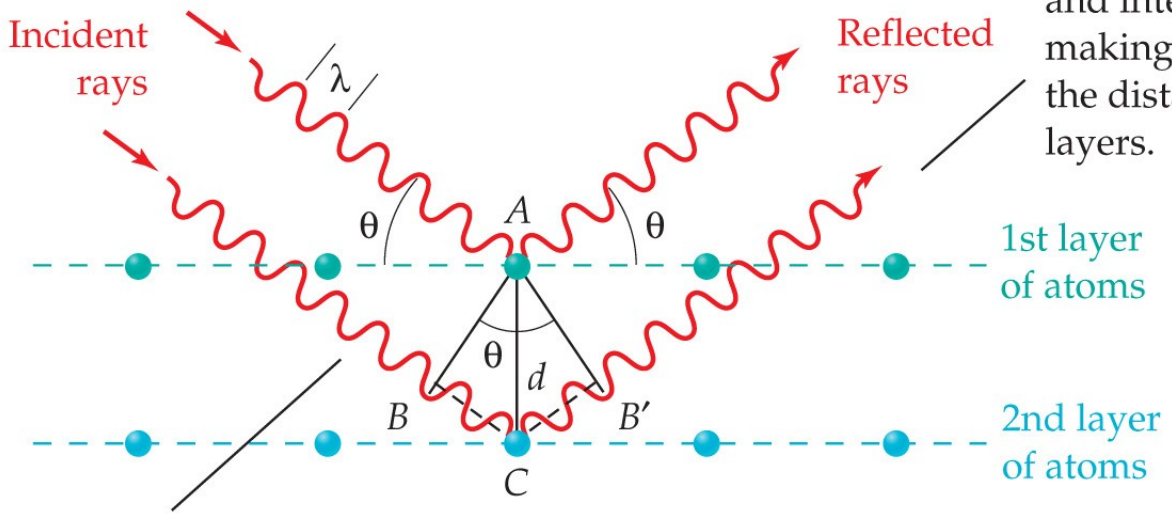


Constructive interference occurs if the waves are in-phase, producing a wave with increased intensity.



Destructive interference occurs if the waves are out-of phase, resulting in cancellation.

Probing the Structure of Solids: X-Ray Crystallography



If the extra distance is a whole number of wavelengths, the reflected rays are in-phase and interfere constructively, making it possible to calculate the distance *d* between the layers.

Rays striking atoms in the second layer travel a distance equal to $BC + CB'$ farther than rays striking atoms in the first layer.

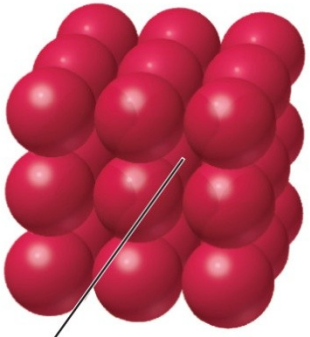
Bragg Equation: $d = \dfrac{n\lambda}{2 \sin \theta}$

Unit Cells and the Packing of Spheres in Crystalline Solids

Simple Cubic Packing

Body-Centered Cubic Packing

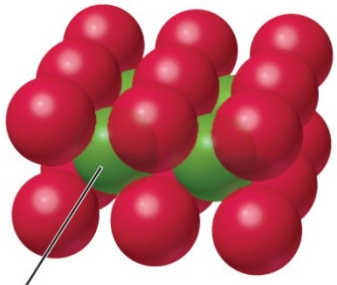
(a) In simple cubic packing, all the layers are **identical** and all atoms are lined up in stacks and rows.



Simple cubic

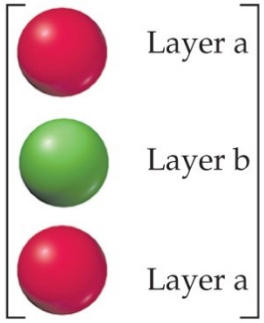
Each sphere is touched by six neighbors, four in the same layer, one directly above, and one directly below.

(b) In body-centered cubic packing, the spheres in **layer** ***a*** are separated slightly and the spheres in **layer** ***b*** are offset so that they fit into the depressions between atoms in layer *a*. The third layer is a repeat of the first.

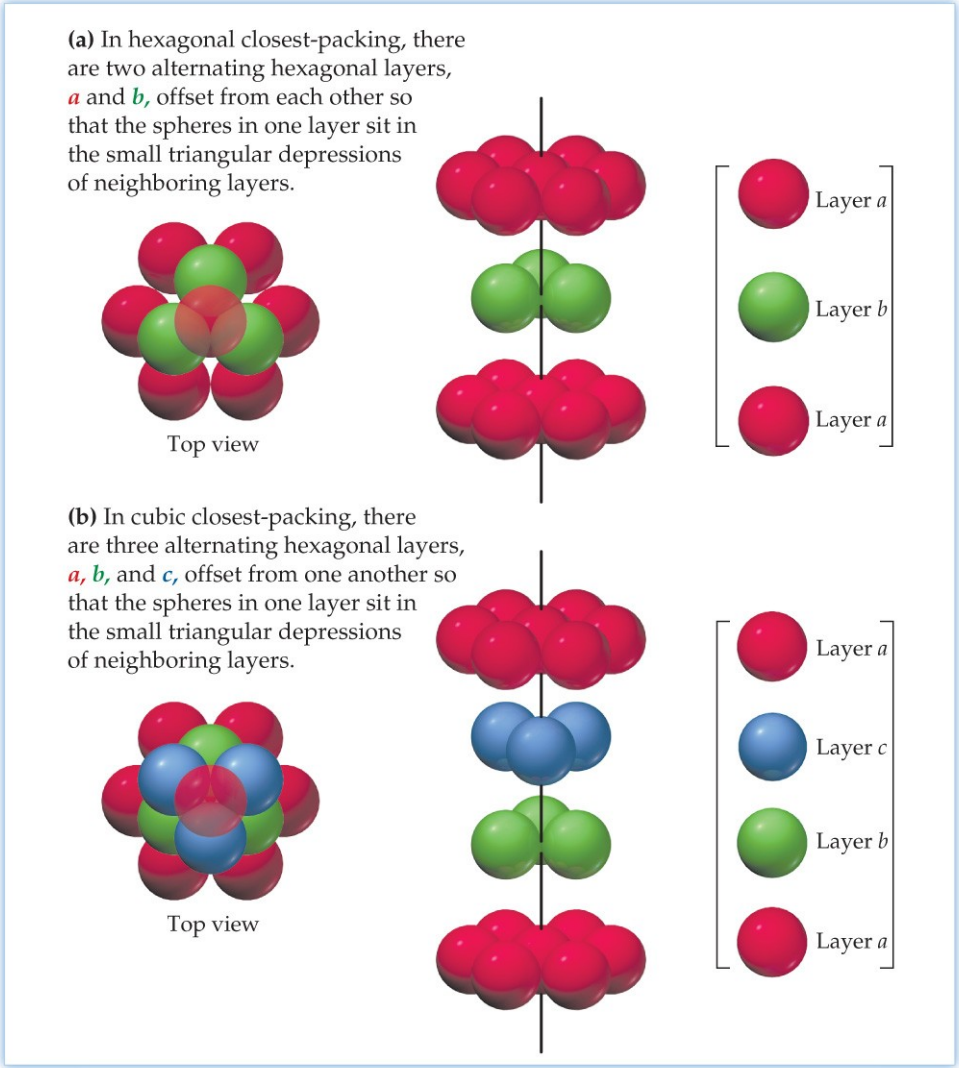


Body-centered cubic

Each sphere is touched by eight neighbors, four in the layer below, and four in the layer above.



Unit Cells and the Packing of Spheres in Crystalline Solids


(a) In hexagonal closest-packing, there are two alternating hexagonal layers, a and b, offset from each other so that the spheres in one layer sit in the small triangular depressions of neighboring layers.
Top view
Layer a
Layer b
Layer a
(b) In cubic closest-packing, there are three alternating hexagonal layers, a, b, and c, offset from one another so that the spheres in one layer sit in the small triangular depressions of neighboring layers.
Top view
Layer a
Layer c
Layer b
Layer a

Hexagonal Closest-Packing

Cubic Closest-Packing

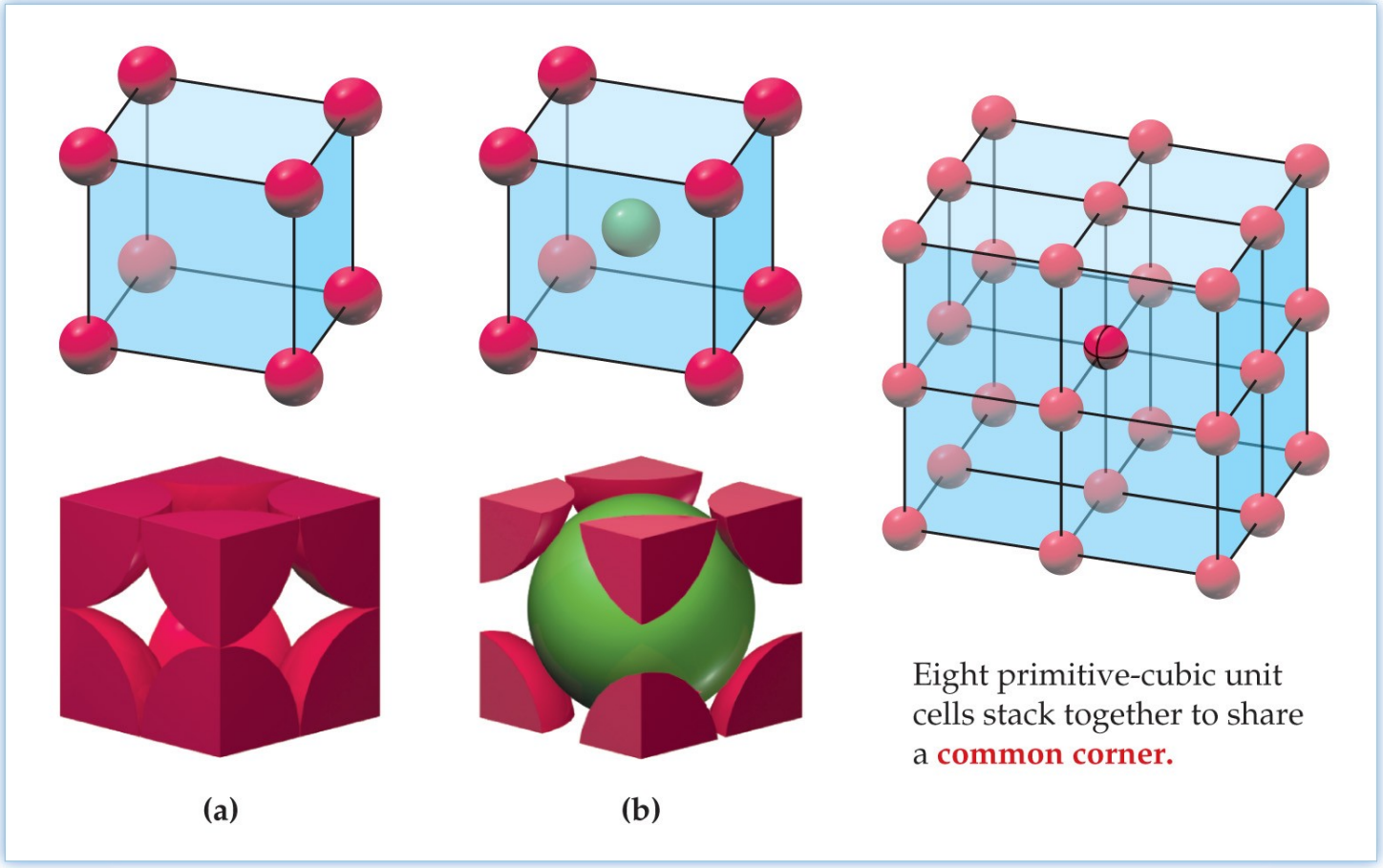
Unit Cells and the Packing of Spheres in Crystalline Solids

Unit Cell: A small repeating unit that makes up a crystal.

Unit Cells and the Packing of Spheres in Crystalline Solids

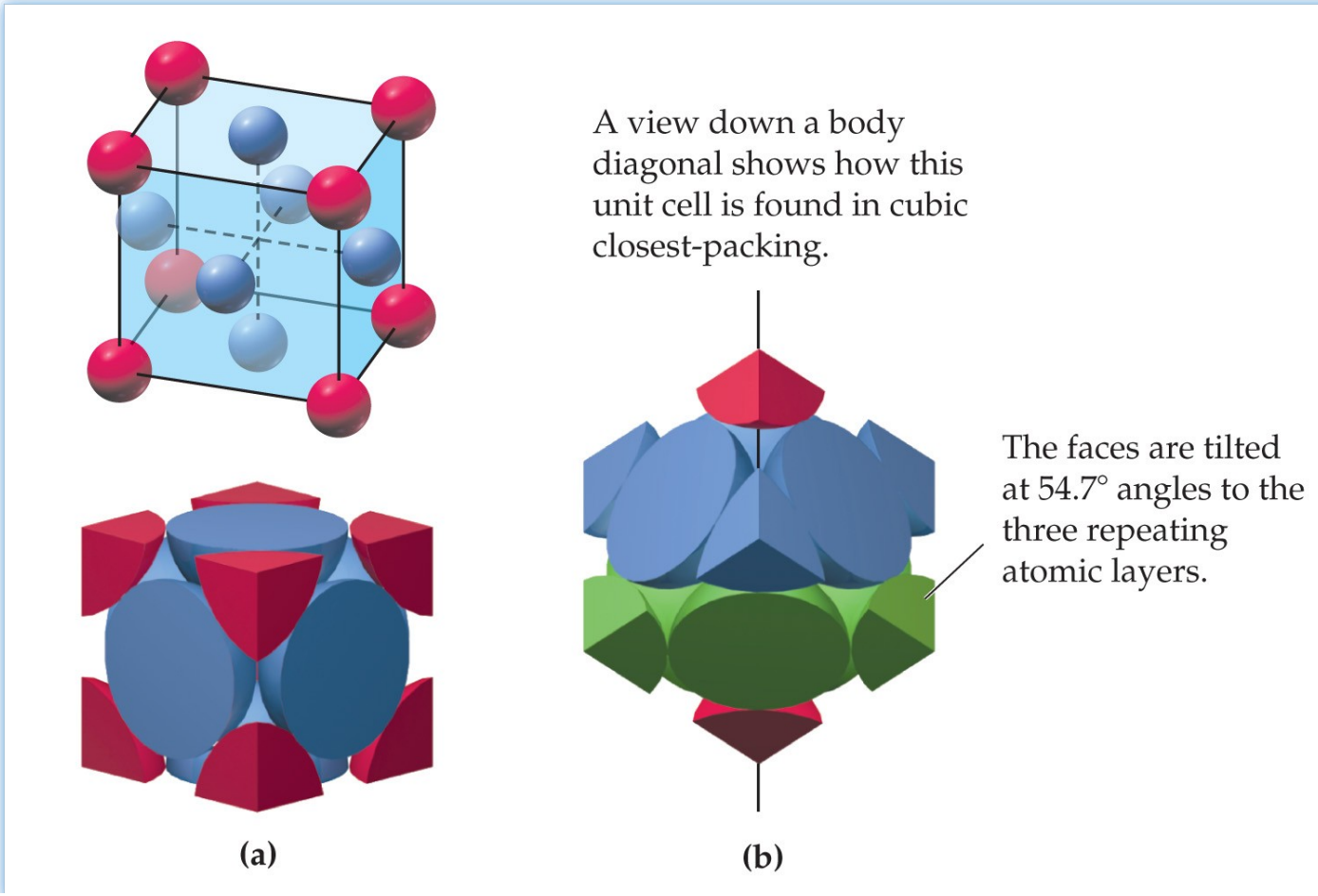
Primitive Cubic

Body-Centered Cubic



Unit Cells and the Packing of Spheres in Crystalline Solids

Face-Centered Cubic

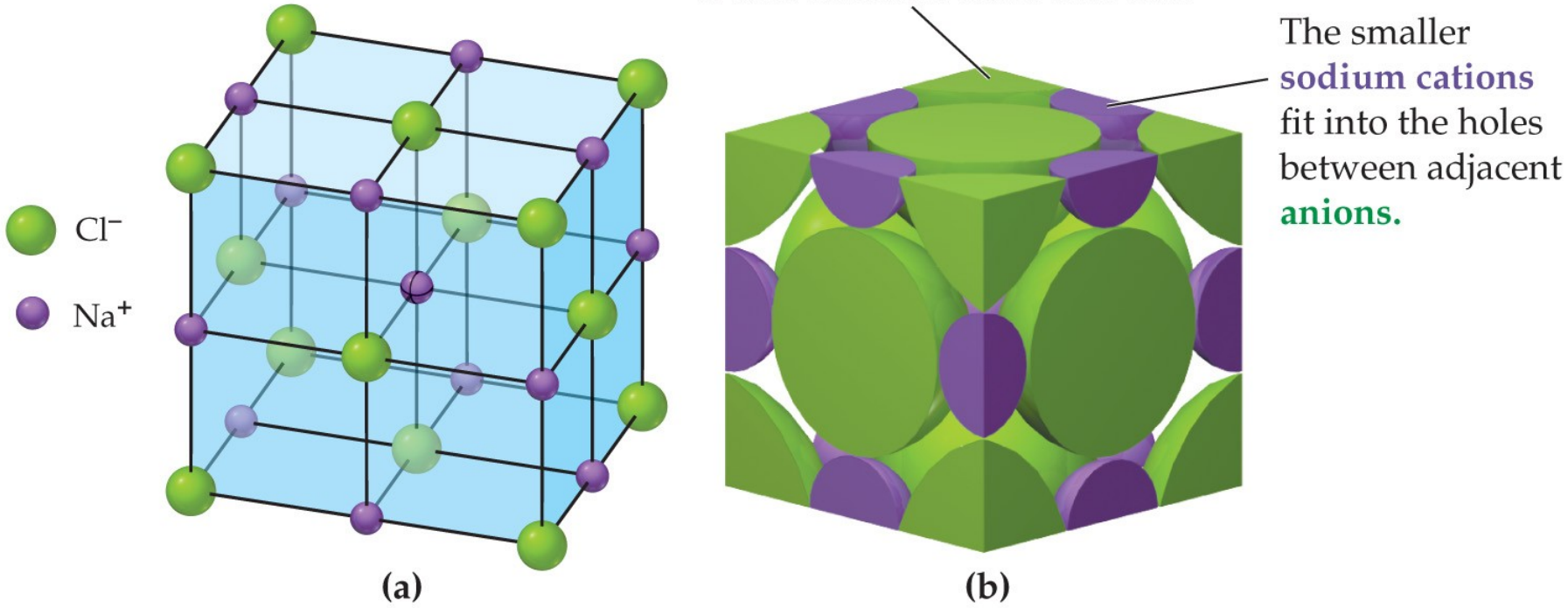

A view down a body diagonal shows how this unit cell is found in cubic closest-packing.
The faces are tilted at 54.7° angles to the three repeating atomic layers.
(a)
(b)

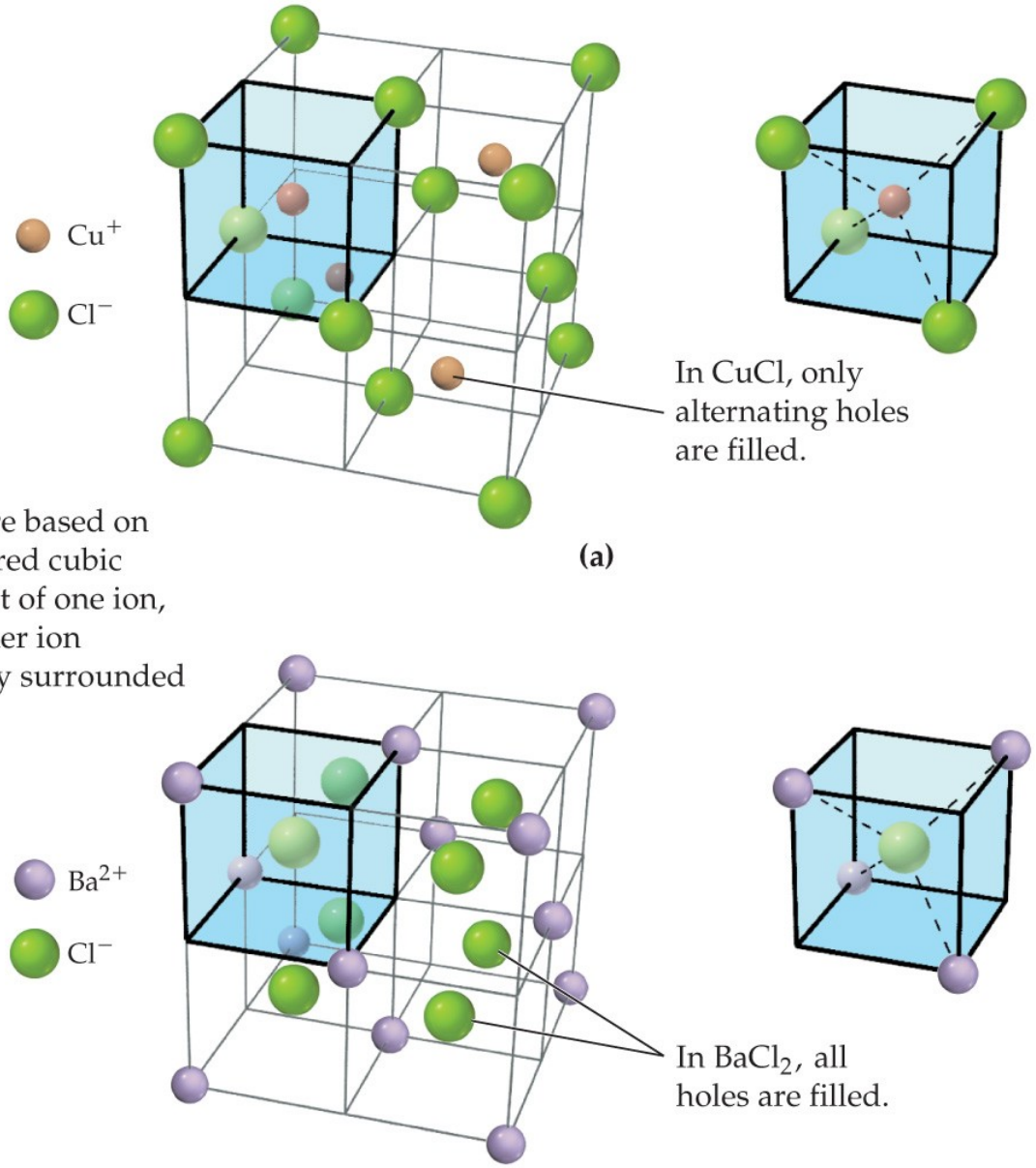
Unit Cells and the Packing of Spheres in Crystalline Solids

TABLE 10.10 Summary of the Four Kinds of Packing for Spheres

Structure	Stacking Pattern	Coordination Number	Space Used (%)	Unit Cell
Simple cubic	*a-a-a-a-*	6	52	Primitive cubic
Body-centered cubic	*a-b-a-b-*	8	68	Body-centered cubic
Hexagonal closest-packed	*a-b-a-b-*	12	74	(Noncubic)
Cubic closest-packed	*a-b-c-a-b-c-*	12	74	Face-centered cubic

Structures of Some Ionic Solids


Cl⁻
Na⁺
(a)
The larger chloride anions adopt a face-centered cubic unit cell.
The smaller sodium cations fit into the holes between adjacent anions.
(b)


Cu^+
Cl^-
In CuCl, only alternating holes are filled.
(a)
Both cells are based on a face-centered cubic arrangement of one ion, with the other ion tetrahedrally surrounded in holes.
Ba^{2+}
Cl^-
In $BaCl_2$, all holes are filled.
(b)

Structures of Some Covalent Network Solids

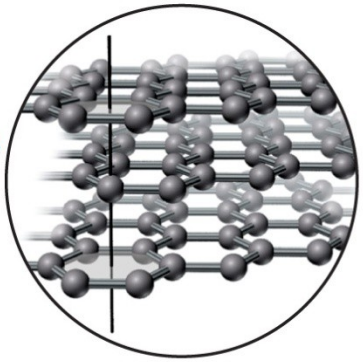
Carbon Allotropes

Allotropes: Different structural forms of an element.

Structures of Some Covalent Network Solids

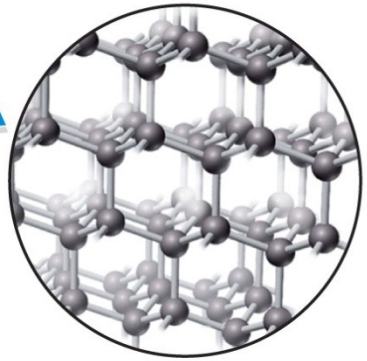
Carbon Allotropes

Graphite is a covalent network solid consisting of two-dimensional sheets of sp^2-hybridized carbon atoms organized into six-membered rings.



The atoms in each sheet are offset slightly from the atoms in neighboring sheets.

(a)

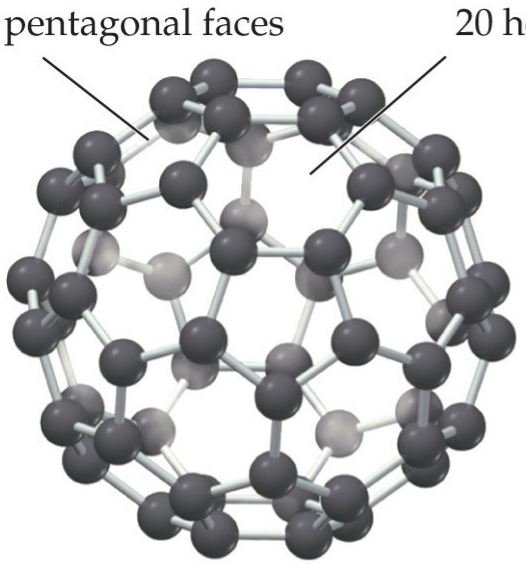


Diamond is a vast, three-dimensional array of sp^3-hybridized carbon atoms, each of which is bonded with tetrahedral geometry to four other carbons.

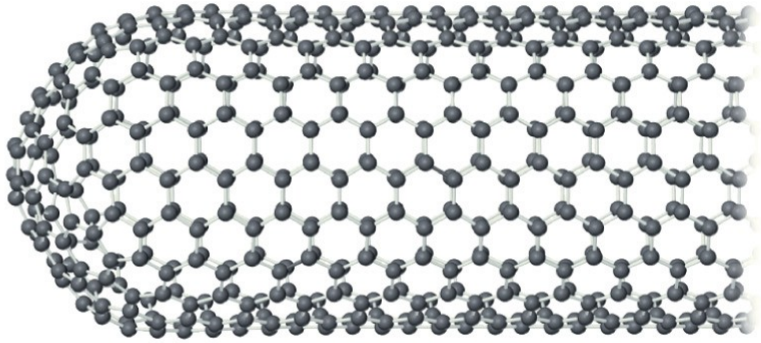
(b)

Structures of Some Covalent Network Solids

Carbon Allotropes



(a) Fullerene is a molecular solid whose molecules have the shape of a soccer ball. The ball has 12 pentagonal and 20 hexagonal faces, and each carbon atom is sp^2-hybridized.

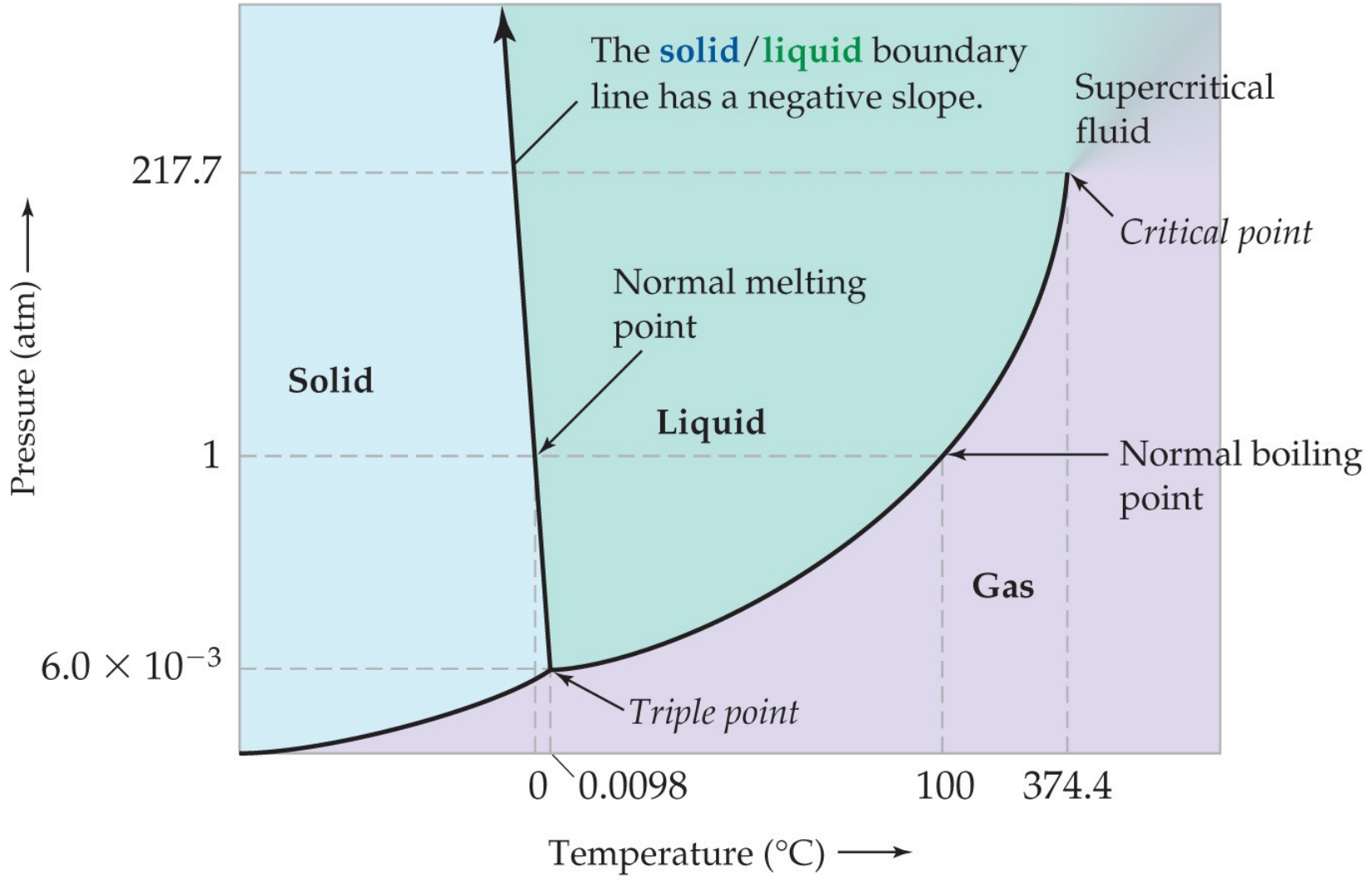


(b) Carbon nanotubes consist of sheets of graphite rolled into tubes of 2–30 nm diameter.

Structures of Some Covalent Network Solids

Silica (SiO_2)

- quartz
- sand
- quartz glass


The solid/liquid boundary line has a negative slope.
Supercritical fluid
Critical point
Normal melting point
Solid
Liquid
Normal boiling point
Gas
Triple point
Pressure (atm)
217.7
1
6.0 × 10−3
0
0.0098
100
374.4
Temperature (°C)

Phase Diagrams

Normal: Occurs at 1 atm.

Critical Point: A combination of temperature and pressure beyond which a gas cannot be liquefied.

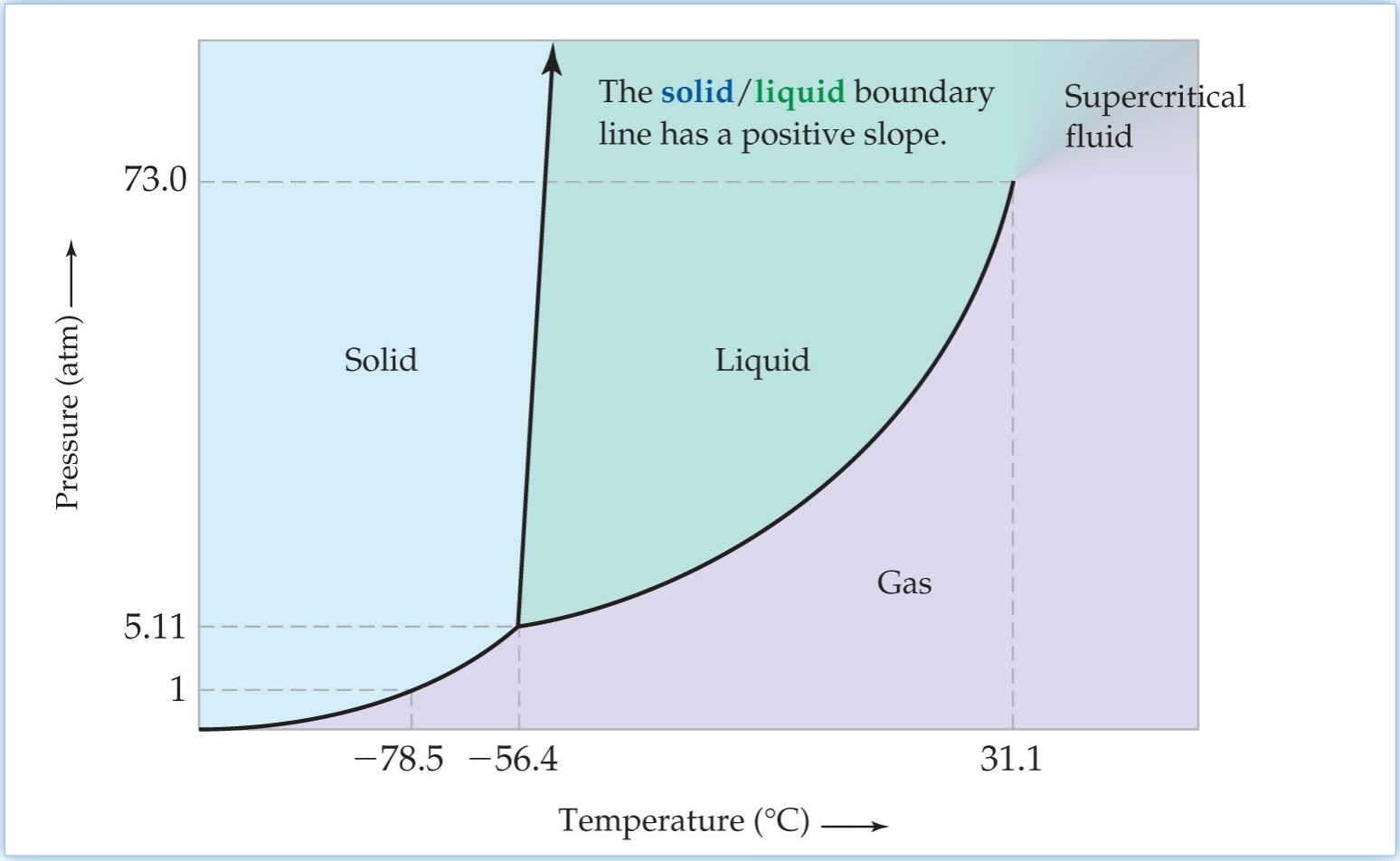
- **Critical Temperature**: The temperature beyond which a gas cannot be liquefied regardless of the pressure.
- **Critical Pressure**: The pressure beyond which a liquid cannot be vaporized regardless of the temperature.

Supercritical Fluid: A state of matter beyond the critical point that is neither liquid nor gas.

Triple Point: A point at which three phases coexist in

Phase Diagrams

Carbon Dioxide



Phase Diagrams

Water